

Adsorption of Colloidal Particles in the Presence of External Fields

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We present a new class of sequential adsorption models in which the adsorbing particles reach the surface following an inclined direction (*shadow models*). Capillary electrophoresis, adsorption in the presence of a shear, and adsorption on an inclined substrate are physical manifestations of these models. Numerical simulations are carried out to show how the new adsorption mechanisms are responsible for the formation of more ordered adsorbed layers and have important implications in the kinetics, in particular, modifying the jamming limit.

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In recent years much interest has been devoted to the study of the adsorption of colloidal particles in solid surfaces [1,2]. In its complete formulation, the process becomes complex because one should take into account the different forces which will influence the rate of the arrival of each particle at the surface, as well as its relative position with respect to the preadsorbed ones [3,4]. Recently, in order to study the adsorption kinetics, attention has been focused mainly on the effect of surface exclusion, accounting for the fact that once a particle is adsorbed it reduces the available surface for further adsorbing ones. For large particles like colloids, such a blocking effect is a nonlinear function of the surface coverage, since the excluded regions of different particles may overlap each other. Two major models have been proposed to take these effects into account. On one hand, in the random sequential adsorption (RSA) model [5,6] if the center of the incoming particle, whose position has been randomly chosen on the surface, overlaps with a previously adsorbed one, it is rejected and a new random position is selected; otherwise, the particle is located irreversibly at that position. Despite its simplicity, experimental results on the adsorption of diffusing latex spheres and polymers seem to agree with its predictions [7,8]. On the other hand, in the ballistic model (BM) [9,10] if the center of the incoming particle overlaps with a previously adsorbed one, it is allowed to roll over it, approaching the surface along the steepest descent path. The particle is rejected only when it cannot reach the surface, otherwise it is irreversibly located at that position as well. This model can describe the kinetics of the adsorption of large particles when gravity is dominant [11].

We will introduce a new class of sequential adsorption models in which particles adsorb according to RSA or BM rules, but reach the surface along an inclined direction. Our goal in this Letter is to show, through a numerical analysis, the new adsorption mechanisms with respect to the ones proposed up to now, and their implications in the different physical properties of the adsorbed layer. In particular, when considering BM rules, nonlocal effects

will appear in the dynamics of the incoming particles, which have important implications in the values of physical quantities. Moreover, this class of models may cover different physical situations of interest. It can correspond either to the adsorption of particles in the presence of an external field acting parallel to the surface or to adsorption on an inclined substrate. Two specific examples of the first case are capillary electrophoresis [12] and adsorption in the presence of an imposed shear for sufficiently small diffusion layers [8,13]. To be precise, we will study the adsorption of disks of diameter l which arrive at the surface forming an angle α with the normal to the line [see Fig. 1(a)]. As shown in the figure, an incident disk cannot land closer than a distance of $l + \sigma = l/\cos\alpha$ to the right of a preadsorbed particle, which can be thought of as though the adsorbed particle projected a shadow on the line which cannot be occupied by an incident particle, therefore changing the overlapping mechanism with respect to the standard models. The different physical situations are considered by studying the relationship between α (or σ) and the corresponding physical parameters of interest.

In order to find out more about the relevant features introduced by these models, we have numerically analyzed the adsorption kinetics of disks on a line of length 1000 diameters. Two major kinds of quantities are of interest in these models: the density of adsorbed particles as a function of time and, in particular, the maximum fraction of the surface covered by the particles, referred to as the *jamming limit* ρ_∞ , and the structure of the adsorbed phase, which follows from the pair distribution function. Those quantities will be studied in two models keeping the rules of the standard RSA and BM.

We will first consider the adsorption of hard disks following RSA rules. For this reason, disks are placed sequentially and randomly on the line. If the chosen position is at a distance smaller than l to the left of a preadsorbed disk or at a distance smaller than $l + \sigma$ to the right of a preadsorbed disk [see Fig. 1(a)], the incoming particle is rejected and a new position is

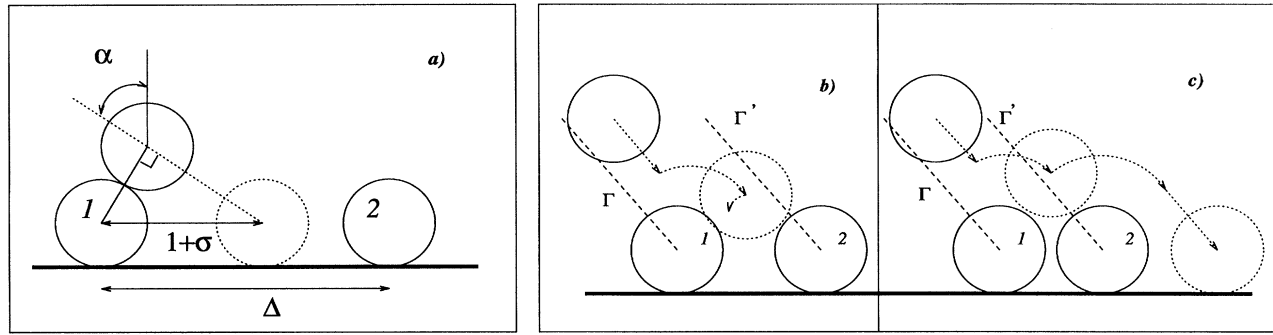


FIG. 1. (a) Trajectory of an incoming particle of diameter unity forming an angle α with the normal to the adsorbing line, in the presence of two adsorbed disks, 1 and 2, at a distance Δ . $1 + \sigma$ represents the minimum distance between a preadsorbed disk and the incoming particle on the line to its right. (b),(c) New adsorption mechanisms in the BM. The incident disk rolls over disk 1 and touches disk 2. (b) If its center is to the left of line Γ' , it rolls to its left as in a standard BM. (c) If its center is to the right of line Γ' , it will reach the line to the right of disk 2. Its kinetics depends now on a third sphere on the line.

chosen; otherwise it is irreversibly located at that position. Therefore the inclined direction of arrival changes the overlapping mechanism with respect to the RSA. It is worth noting that the relationship between the angle and the excluded length makes it possible to consider the system as if we had incoming particles of length 1 which, upon arrival at the surface, deformed a length $1 + \sigma$ towards the right. This asymmetry in the deformation makes these models different from the restructuring-particle RSA proposed in the literature to study the adsorption of certain proteins which deform at the surface [14]. In Fig. 2 we show the jamming limit as a function of σ compared to its corresponding analytical expression

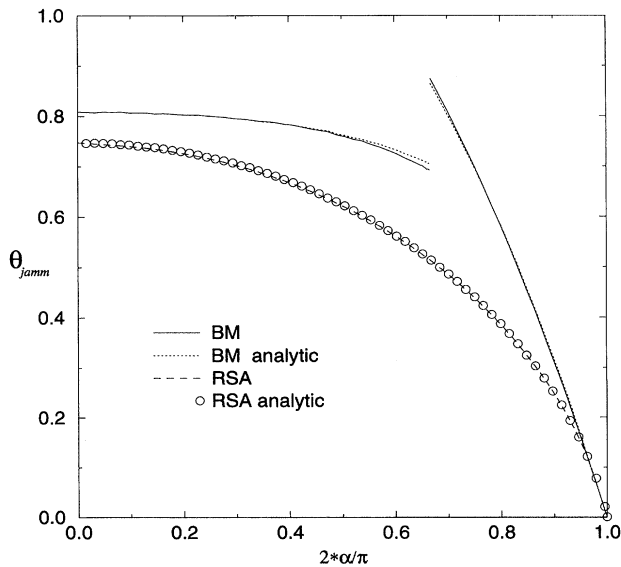


FIG. 2. Jamming limit as a function of $2\alpha/\pi$ for RSA (---) and BM (—) numerical. Analytically, RSA (ooo) and BM (···).

$$\rho(t)^{\text{RSA}} = \int_0^t \exp\left[\int_0^\tau (-2 + e^{-u} + e^{-(1+\sigma)u}) \frac{du}{u}\right] d\tau \tag{1}$$

by taking the limit $t \rightarrow \infty$, which has been obtained from the corresponding integro-differential equations along the same lines as in the standard RSA [6]. An analysis of the asymptotic behavior of Eq. (1) gives $\rho_\infty^{\text{RSA}} - \rho(t)^{\text{RSA}} \sim 1/(1 + \sigma)t$ for long times. Details about the deduction of Eq. (1) will be presented elsewhere. As the incident angle α increases, the jamming decreases considerably, since lengths between adsorbed disks smaller than $1 + \sigma$ cannot be occupied. The structure of the adsorbed disks is also modified. As seen in Fig. 3(a), the pair distribution function at jamming exhibits two peaks located at $r = 1$ and $r = 1 + \sigma$. The former corresponds to the usual peak when particles are in contact, whereas the latter results from the fact that now $1 + \sigma$ is a new minimum distance between particles. A careful theoretical analysis shows that both peaks are similar in shape, therefore the second peak also diverges logarithmically at jamming.

In the second case, we will study the adsorption of disks according to BM rules. Again, positions are sequentially selected at random. If a chosen position overlaps disk 1 on the left hand side of line Γ [see Fig. 1(b)], the particle will roll to the left and will end up on the line at contact with the preadsorbed disk. However, if it is on the right hand side of that line at a distance smaller than $1 + \sigma$, it will end up at a separation $1 + \sigma$ on the surface. Therefore the probability that an incoming disk will end at a length $1 + \sigma$ to the right of a previously adsorbed one is greater than the probability of landing at a distance 1 on its left hand side. This modified overlapping introduces significant changes in the behavior of the incoming particle when there exists an interaction with a second adsorbed disk. In particular, new restructuring effects appear with respect to the standard BM.

In fact, consider two particles at a distance $\Delta < 2 + \sigma$, and an incoming disk overlapping the left one to the

right of line Γ [see Fig. 1(b)]. When the disk comes into contact with particle 1, it will roll over it trying to reach a position at the surface at a distance $1 + \sigma$ from it. During its motion, it can touch disk 2 before reaching the wall. Then, if the center of the incoming disk is to the left of line Γ' , the particle will try to reach the surface to the left of disk 2, if space is available [Fig. 1(b)]. However, if its center is to the right of that line, the incoming disk will try to reach the surface at a distance $1 + \sigma$ on the right hand side of disk 2 [Fig. 1(c)]. As a result, the motion of the incoming particle will depend on a third preadsorbed disk to the right of disk 2. Therefore the incoming disk may jump over a number of adsorbed particles before reaching a place at the surface. This nonlocal adsorption mechanism cannot take place in standard BM, since only when $\alpha \geq \pi/6$ may the center of the incoming disk be to the right of Γ' after rolling over particle 1. When $\sigma \geq 1$ ($\alpha \geq \pi/3$) the adsorption process exhibits two new properties. On one hand, there will be no rejected particles before reaching jamming because the incoming disks will always jump over small gaps until they reach an available space on the line. On the other hand, when $\Delta = 1 + \sigma$, a new singular contribution to the dynamics appears because all particles rolling to the right over disk 1 will reach disk 2 at the line Γ' . Assuming that those disks then roll to its left, e.g., due to gravity, they will end up at contact with disk 2 to the right of disk 1.

In Fig. 2 we have plotted the jamming density as a function of α . At $\alpha = \pi/3$, a jump in the jamming density is observed due to the singular contribution of gaps of length $\Delta = 1 + \sigma$ in which now we may accommodate a new disk. The magnitude of the jump equals the fraction of disks which reach the line following the new rolling mechanism explained before. It is possible to obtain an analytical expression for the deposition according to BM rules, which takes the singular contribution into account, but which neglects the nonlinear adsorption mechanism

discussed previously. For $\alpha < \pi/3$ it gives

$$\rho(t)^{\text{BM}} = \int_0^t d\tau \frac{d\rho^{\text{RSA}}(\tau)}{d\tau} (2\tau + 1) e^{-2\tau} e^{2-e^{-\tau}-e^{-(1+\sigma)\tau}}. \quad (2)$$

This analytic model is exact for $\alpha \leq \pi/6$, and gives an accurate estimate of the jamming at larger angles, as shown in Fig. 2. This last feature explains the differences observed in the jamming coverage near $\alpha = \pi/3$. For $\alpha \geq \pi/3$, the coverage increases linearly in time until jamming, since there are no rejected particles, and when $\alpha \leq \pi/3$, inspection of the analytical result leads to the asymptotic time behavior $\rho_\infty^{\text{BM}} - \rho(t)^{\text{BM}} \sim \exp(-t)/t$.

In Fig. 3(b) we show the pair distribution function at jamming. The peaks observed correspond to clusters of particles, which originate from the rolling mechanisms. The separation between disks in a given cluster is 1 or $1 + \sigma$ (and also $\sigma - 1$, if $\sigma \geq 1$). Therefore the number of peaks increases at distances in multiples of the diameter, since particles can be distributed in two different sets of lengths which are incommensurable when σ is irrational. For example, for $\sigma = 0.165$, we observe two peaks near $r = 1$, corresponding to separations $r = 1$ and $r = 1 + \sigma$, three peaks near $r = 2$, corresponding to distances $r = 2$, $r = 2 + \sigma$, and $r = 2(1 + \sigma)$, and so on. The relative areas under the peaks are equal to the relative probabilities for each configuration of disks. When $\sigma = 1$, both kinds of distances are commensurable, so when two particles are separated by $1 + \sigma$, there is exactly enough room for another particle, and therefore an ordered sequence of peaks is obtained. Moreover, for $\sigma \geq 1$ the number of peaks increases also due to the new singular contribution. It should be noted that the larger the value of σ , the more ordered the structure of the adsorbed layer, the reason being that when increasing σ the probability of being at a distance $1 + \sigma$ increases relative to that at a distance 1 from a preadsorbed disk.

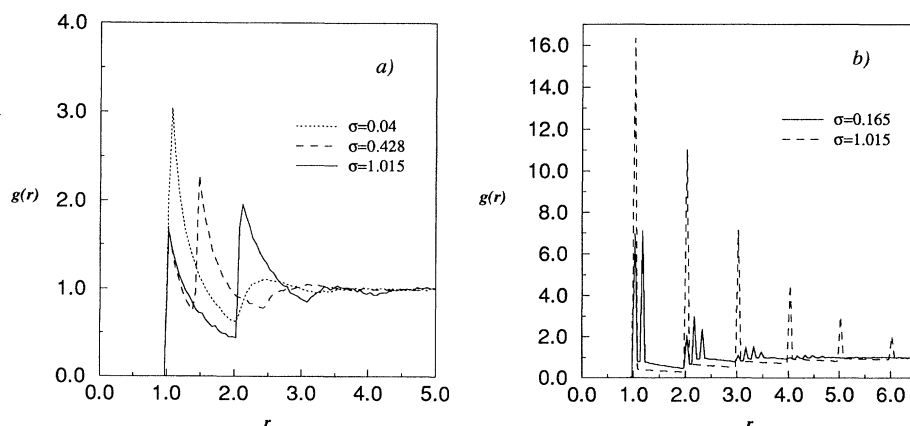


FIG. 3. The function $g(r)$ for (a) RSA at $\sigma = 0.04$ (\cdots), 0.428 ($- -$), and 1.015 ($-$). (b) BM at $\sigma = 0.165$ ($-$) and 1.015 ($- -$).

In summary, we have introduced two new kinetic models (*shadow models*) to study the adsorption of disks on a line taking into account a driving in the direction parallel to the surface. New adsorption mechanisms which may take place have been shown, as well as their effects both in the jamming coverage and in the pair distribution function. In particular, when considering BM rules, we have shown that for angles larger than $\pi/3$ incident disks may roll over a number of preadsorbed particles before reaching the line, which means that the kinetics have become nonlocal. Moreover, for both BM and RSA rules, this driving originates more ordered substrates on the lines, as shown through the pair correlation functions.

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